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Reactions of (Arylimido)vanadium(V)−Trialkyl Complexes with Phenols: Effects of Arylimido Ligands and Phenols for Formation of the Vanadium Phenoxides

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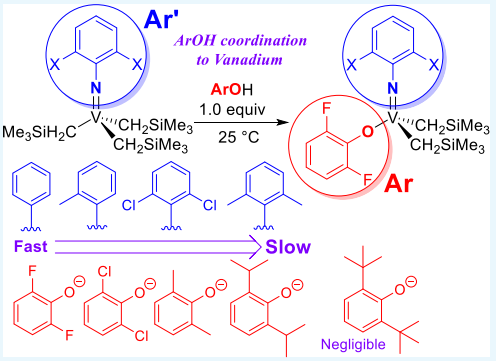
Supporting Information

ABSTRACT: Reactions of a series of (arylimido)vanadium(V) trialkyl complexes, V(NAr′)(CH_2SiMe_3)$_3$ (Ar′ = C_6H_5, 2-MeC_6H_4, 2,6-$Me_2C_6H_3$, 2,6-$Cl_2C_6H_3$), with various phenols (ArOH, Ar = 2,6-$F_2C_6H_3$, 2,6-$Cl_2C_6H_3$, 2,6-$Me_2C_6H_3$, 2,6-$^iPr_2C_6H_3$, 2-^{t}BuC_6H_4, 2,6-^{t}Bu$_2C_6H_3$; 1.0 equiv) affording V(NAr′)(CH_2SiMe_3)$_2$(OAr) were conducted in C_6D_6 at 25 °C, and the effects of both arylimido ligands and phenols on the substitution rate were explored. Sterically hindered arylimido ligands showed lower reactivity, and the reaction proceeded in the order: Ar′ = 2,6-$Me_2C_6H_3$ < 2,6-$Cl_2C_6H_3$ < 2-MeC_6H_4 < C_6H_5. This order is somewhat different from that obtained from the chemical shifts in V(NAr′)(CH_2SiMe_3)$_3$ in the ^{51}V NMR spectra. The conversions with various disubstituted phenols increased in the order: 2,6-$^iPr_2C_6H_3$OH < 2,6-$Me_2C_6H_3$OH < 2,6-$Cl_2C_6H_3$OH < 2,6-$F_2C_6H_3$OH, irrespective of the kind of arylimido ligands. The reactions of V(NAr′)(CH_2SiMe_3)$_3$ with 2,6-^{t}Bu$_2C_6H_3$OH (1.0 or 3.0 equiv) did not take place even upon heating at 60 °C. These results suggest that the reactions proceed via coordination of ArOH toward vanadium, and the reactivity is highly dependent on steric bulk of both the arylimido ligand and the phenol.



INTRODUCTION

Transition-metal alkyl complexes are among the most important reagents or intermediates in organic reactions,[1−4] and the study of their reaction chemistry has been recognized as an important subject for better understanding especially in catalysis cycles, reaction pathways, and design of efficient catalysts.[1−4] The metal alkyl species play a key role in olefin polymerization, the core technology for the production of polyolefins in the chemical industry.[5−18] Since classical Ziegler type vanadium catalyst systems display unique characteristics (highly reactive toward olefins exemplified as production of ultrahigh molecular weight polyethylene with narrow molecular weight distributions),[19−21] the reaction chemistry of vanadium−alkyl complexes[22−38] should be considered as an important subject in the field of catalysis[12,38−41] and organometallic chemistry.[42−44]

Early transition-metal−alkyl bonds have been known to be more nucleophilic than those with late transition metals, and these are thus highly reactive toward Brönsted/Lewis acids.[1−5] For example, cationic alkyl complexes, proposed active species for olefin polymerization, are formed by treating the dialkyl analogues with Al alkyls or borate through protonolysis or alkyl abstraction.[5−18,40,41] These metal alkyls are generally rapidly reacted with alcohols (or phenols, ArOH) via protonation or coordination and a subsequent hydrogen transfer pathway (Scheme 1). It has been, however, reported that steric crowding in tetrakis(alkyl)-chromium(IV)[45,46] and zirconium(IV)[47] complexes [exemplified as Cr^{t}Bu$_4$ and Zr($CH_2{}^t$Bu)$_4$] and (arylimido)vanadium(V) trialkyl complex (described below)[48] contributes to greater stability toward oxygen and alcohols. For example, Wolczanski et al.[47] reported that the synthesis of Zr($CH_2{}^t$Bu)$_3$(OC^tBu$_3$) from Zr($CH_2{}^t$Bu)$_4$ by treating with ^{t}Bu$_3$COH (1.61 equiv) in benzene required 30 h under reflux conditions (93−95 °C), whereas the synthesis of Zr(CH_2Ph)$_3$(OC^tBu$_3$) from Zr(CH_2Ph)$_4$ with ^{t}Bu$_3$COH (1.14 equiv) required only 7 h.[47]

Moreover, the reaction of V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_3$ with excess 2,6-^{t}Bu$_2$-4-MeC_6H_2OH (2.6 equiv) in $C_2D_2Cl_4$ at 50 °C did not take place, whereas most reactions of V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_3$ with 1.0 equiv of less sterically hindered phenols and alcohols afforded the corresponding dialkyl complexes exclusively at 25 °C (Scheme 2).[48] Synthesis of V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)(O-2,6-$Me_2C_6H_3$)$_2$ from V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_2$(O-2,6-$Me_2C_6H_3$) by treating with 2,6-$Me_2C_6H_3$OH required 50 h at 60 °C for completion, and the reaction did not take place (or was too slow) at 25 °C. In contrast, immediate phenoxide ligand exchange was observed when V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_2$(O-2,6-$Me_2C_6H_3$) was treated with 1.0 equiv of C_6F_5OH at 25 °C (Scheme 2).[49] These results thus suggest a reaction mechanism by coordination of phenols on the vanadium metal center (Scheme 2, shown in brackets) and not by protonation. It has also been assumed that

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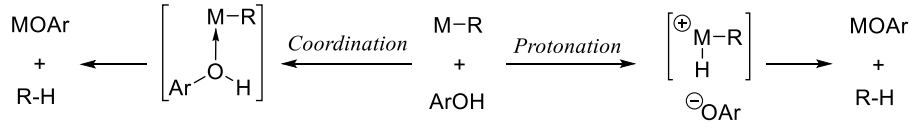
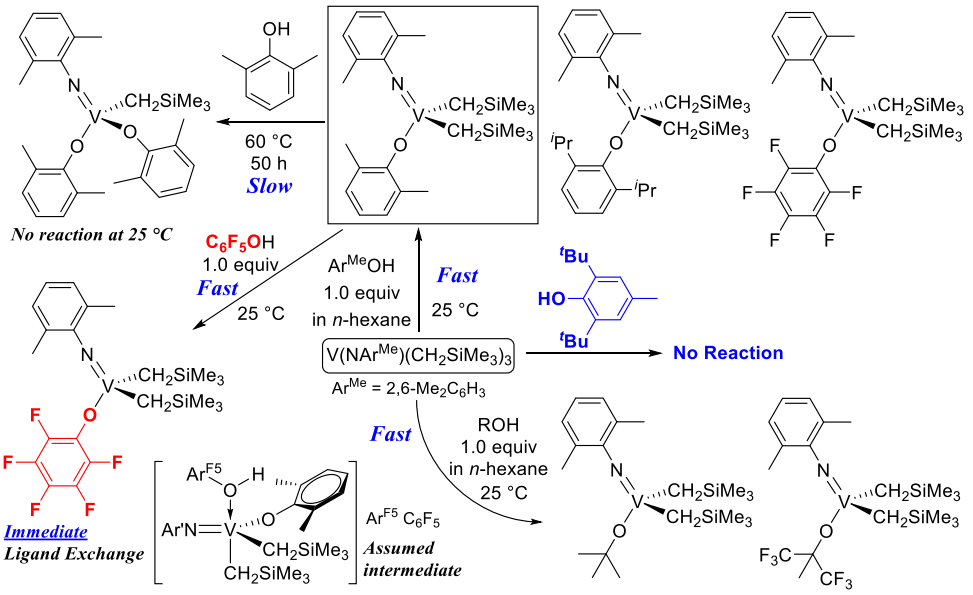
Scheme 1. Two Probable Pathways for Reaction of Metal Alkyl with Phenol (ArOH)



Scheme 2. Reactions of $V(N\text{-}2,6\text{-}Me_2C_6H_3)(CH_2SiMe_3)_3$ with Phenols, Alcohols,[48] and Fast Phenoxy Ligand Exchange in $V(N\text{-}2,6\text{-}Me_2C_6H_3)(CH_2SiMe_3)_2(O\text{-}2,6\text{-}Me_2C_6H_3)$[49]

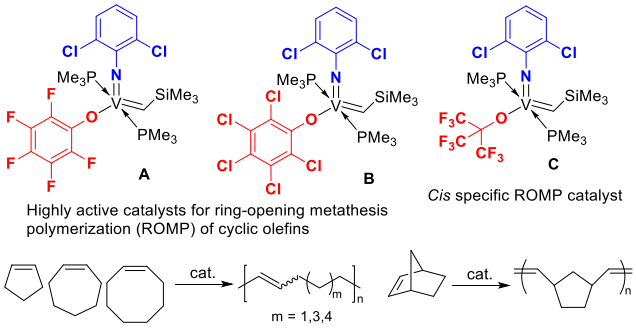


the reason for the negligible reactivity of 2,6-^{t}Bu$_2$-4-MeC$_6$H$_2$OH could be due to a steric bulk of two *tert*-butyl groups and three CH_2SiMe_3 ligands that causes a difficulty of coordination of the phenol to vanadium. Similarly, the reaction of $V(CHSiMe_3)(N\text{-}1\text{-adamantyl})(CH_2SiMe_3)(PMe_3)_2$ with C_6F_5OH became slow when C_6F_5OD was used instead of C_6F_5OH or in presence of PMe_3.[50] The results also suggest the mechanism by coordination of C_6F_5OH accompanied by dissociation of PMe_3.[50,51] However, factors affecting the substitution rates (the electronic nature of phenol or vanadium metal center, steric bulk for coordination of phenol to vanadium, etc.) have still been unclear.

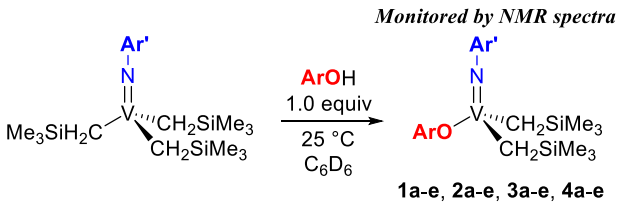
(Arylimido)vanadium(V)−alkylidene complexes containing phenoxide or alkoxide ligands have been known to display promising characteristics as catalysts for ring-opening metathesis polymerization of cyclic olefins (Scheme 3).[42−44,48,50,52−55] These complexes are prepared from the corresponding dialkyl complexes by α-hydrogen elimination in the presence of PMe_3. The dialkyl complexes are prepared from the corresponding trialkyl complexes, $V(NAr')(CH_2SiMe_3)_3$, by treating with 1.0 equiv of phenol or alcohol.

In this study, reactions of a series of (arylimido)vanadium(V) trialkyl complexes, $V(NAr')(CH_2SiMe_3)_3$ (Ar′ = C_6H_5, 2-MeC_6H_4, 2,6-$Me_2C_6H_3$, 2,6-$Cl_2C_6H_3$), with various phenols, ArOH (Ar = 2,6-$F_2C_6H_3$, 2,6-$Cl_2C_6H_3$, 2,6-$Me_2C_6H_3$, 2,6-^{i}Pr$_2$C$_6$H$_3$, 2-^{t}BuC$_6$H$_4$, 2,6-^{t}Bu$_2$C$_6$H$_3$) have been conducted to explore factors (the electronic or steric nature of arylimido ligand or phenol) affecting the reaction rate for affording the phenoxide complexes, $V(NAr')(CH_2SiMe_3)_2(OAr)$ (Scheme 4), which have been prepared and identified independently. The results should provide important information for a better basic understanding of the reaction of high oxidation state early transition-metal-alkyls with phenol, which can be proposed to proceed via coordination of phenol to the metal center.[48,49]

Scheme 3. (Arylimido)vanadium(V)−Alkylidene Complexes as Effective Catalysts for Ring-Opening Metathesis Polymerization[42−44,52−55]



Scheme 4. Reactions of a Series of (Arylimido)vanadium(V)−Trialkyl Complexes with Different Phenols



Ar' = C_6H_5 (**1**), 2-MeC_6H_4 (**2**), 2,6-$Me_2C_6H_3$ (**3**), 2,6-$Cl_2C_6H_3$ (**4**)
Ar = 2,6-$F_2C_6H_3$ (**a**), 2,6-$Cl_2C_6H_3$ (**b**), 2,6-$Me_2C_6H_3$ (**c**), 2,6-^{i}Pr$_2$C$_6$H$_3$ (**d**), 2-^{t}BuC$_6$H$_4$ (**e**)

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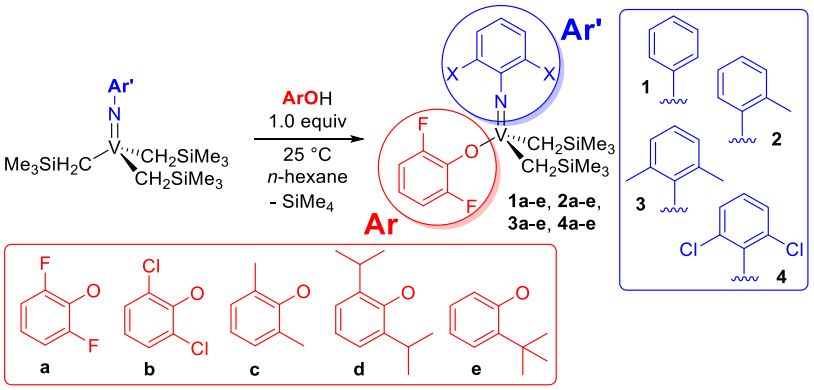
Scheme 5. Synthesis of $V(NAr')(CH_2SiMe_3)_2(OAr)$ [1a−e, 2a−e, 3b,e, 4a−e; Ar′ = C_6H_5 (1), 2-MeC_6H_4 (2), 2,6-$Me_2C_6H_3$ (3), 2,6-$Cl_2C_6H_3$ (4); Ar = 2,6-$F_2C_6H_3$ (a), 2,6-$Cl_2C_6H_3$ (b), 2,6-$Me_2C_6H_3$ (c), 2,6-$^i Pr_2C_6H_3$ (d), 2-$^t BuC_6H_4$ (e)], by reaction of $V(NAr')(CH_2SiMe_3)_3$ with 1.0 equiv of ArOH



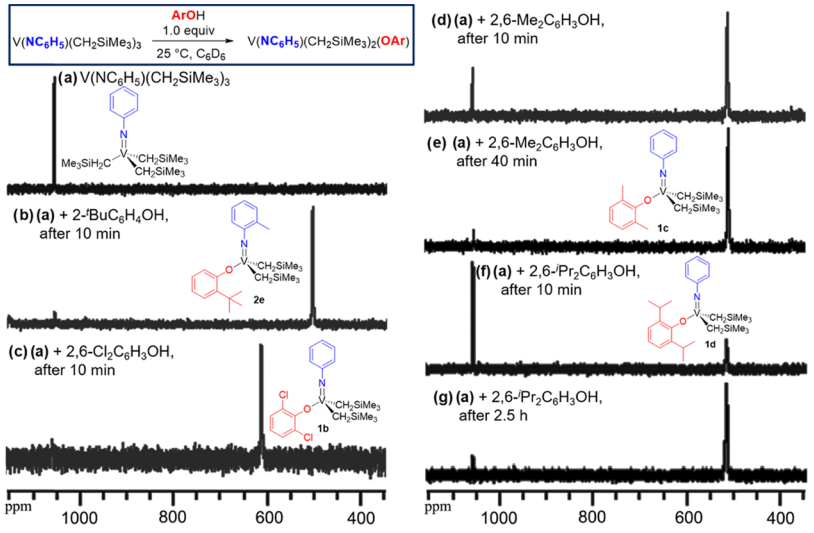


Figure 1. ^{51}V NMR spectra (in C_6D_6 at 25 °C) for monitoring the reaction of $V(NC_6H_5)(CH_2SiMe_3)_3$ with 1.0 equiv of ArOH (2-$^t BuC_6H_4OH$, 2,6-$Cl_2C_6H_3OH$, 2,6-$Me_2C_6H_3OH$, 2,6-$^i Pr_2C_6H_3OH$). Reaction of (a) $V(NC_6H_5)(CH_2SiMe_3)_3$ with (b) 2-$^t BuC_6H_4OH$ (after 10 min, conv. 95%), (c) 2,6-$Cl_2C_6H_3OH$ (after 10 min, conv. 92%), (d) 2,6-$Me_2C_6H_3OH$ (after 10 min, conv. 82%), (e) 2,6-$Me_2C_6H_3OH$ (after 40 min, conv. 95%), (f) 2,6-$^i Pr_2C_6H_3OH$ (after 10 min, conv. 34%), and (g) 2,6-$^i Pr_2C_6H_3OH$ (after 2.5 h, conv. 94%). The conversions (conv.) were estimated on the basis of integration ratios of dialkyl/trialkyl complexes in the ^{51}V NMR spectra (except in the reaction with 2,6-$Cl_2C_6H_3OH$).[b]

RESULTS AND DISCUSSION

Synthesis of (Arylimido)vanadium(V)−Dialkyl Complexes Containing Phenoxide Ligands, $V(NAr')(CH_2SiMe_3)_2(OAr)$. A series of (arylimido)vanadium(V)−dialkyl complexes containing phenoxide ligands, $V(NAr')(CH_2SiMe_3)_2(OAr)$ [**1a−e**, **2a−e**, **3b,e**, **4a−e**; Ar′ = C_6H_5 (**1**), 2-MeC_6H_4 (**2**), 2,6-$Me_2C_6H_3$ (**3**), 2,6-$Cl_2C_6H_3$ (**4**); Ar = 2,6-$F_2C_6H_3$ (**a**), 2,6-$Cl_2C_6H_3$ (**b**), 2,6-$Me_2C_6H_3$ (**c**), 2,6-$^i Pr_2C_6H_3$ (**d**), 2-$^t BuC_6H_4$ (**e**)], could be prepared from $V(NAr')(CH_2SiMe_3)_3$ by treating with 1.0 equiv of ArOH in *n*-hexane at −30 to 25 °C (Scheme 5, synthetic details are shown in the Experimental Section). These synthetic procedures are analogous to those reported previously for syntheses of **3a,c,d**,[48,49] and the resultant complexes were identified by NMR spectra (shown in the Supporting Information, SI)[a] and elemental analysis (except for **3b**, **4d**, and **4e**). Structure of $V(N\text{-}2,6\text{-}Cl_2C_6H_3)(CH_2SiMe_3)_2(O\text{-}2,6\text{-}^i Pr_2C_6H_3)$ (**4d**) was also confirmed by X-ray crystallography (detailed analysis and selected bond distances and angles are shown in the SI).[a] Complex **4d** holds a distorted tetrahedral geometry around vanadium, and the V−N−C(phenyl) bond angle [167.59(11)°] is relatively close to that of $V(N\text{-}2,6\text{-}^i Pr_2C_6H_3)(CH_2Ph)_3$ [**5**, 169.0(5)°][32] but is larger than that of $V(N\text{-}2,6\text{-}^i Pr_2C_6H_3)(CH_2Ph)_2(O\text{-}2,6\text{-}^i Pr_2C_6H_3)$ [**6**, 161.7(4)°];[32] the angle is however smaller than that in $V(N\text{-}1\text{-adamantyl})(CH_2SiMe_3)_3$ [**7**, 180.00(17)°].[a] The V−N bond distance [1.6627(16) Å] is close to that in **6** [1.669(5) Å][32] but longer than that in **5** and **7** [1.641(6), 1.6317(14) Å, respectively].,[32a] The V−O bond distance in **4d** [1.7662(12) Å] is slightly longer than that in **6** [1.746(4) Å],[32] and the V−C bond distance [2.0269(19), 2.019(2) Å] is shorter than that in **5** and **6** [2.048(7)-2.086(8) Å][32] but close to that in complex **7** [2.0267(18) Å].[a]

In contrast, as described below, attempted reactions of $V(NAr')(CH_2SiMe_3)_3$ (Ar′ = C_6H_5, 2-MeC_6H_4, 2,6-$Me_2C_6H_3$, 2,6-$Cl_2C_6H_3$) with 3.0 equiv of 2,6-$^t Bu_2C_6H_3OH$ in C_6D_6 at 25 °C recovered the trialkyl complexes (data are shown in the SI),[b] as reported in the reaction of $V(N\text{-}2,6\text{-}Me_2C_6H_3)(CH_2SiMe_3)_3$ with 2,6-$^t Bu_2$-4-MeC_6H_2OH.[48]

NMR Study for Monitoring Reactions of (Arylimido)-vanadium(V)−Trialkyl Complexes, $V(NAr')(CH_2SiMe_3)_3$, with Phenols (ArOH). Reactions of a series of (arylimido)-

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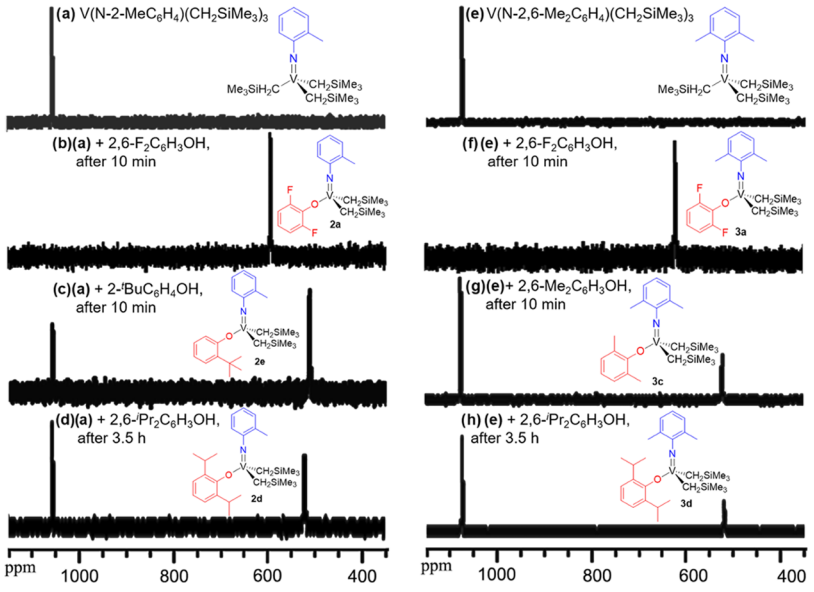

Figure 2. ^{51}V NMR spectra (in C_6D_6 at 25 °C) for monitoring the reaction of V(NAr′)$(CH_2SiMe_3)_3$ with phenols. Reactions of (a) V(N-2-MeC_6H_4)$(CH_2SiMe_3)_3$ with 1.0 equiv of (b) 2,6-$F_2C_6H_3OH$ (after 10 min, conv. >99%), (c) 2-^{t}BuC_6H_4OH (after 10 min, conv. 74%), and (d) 2,6-^{i}Pr$_2C_6H_3OH$ (after 3.5 h, conv. 63%). Reactions of (e) V(N-2,6-$Me_2C_6H_3$)$(CH_2SiMe_3)_3$ with (f) 2,6-$F_2C_6H_3OH$ (after 10 min, conv. >99%), (g) 2,6-$Me_2C_6H_3OH$ (after 10 min, conv. 37%), and (h) 2,6-^{i}Pr$_2C_6H_3OH$ (after 3.5 h, conv. 34%). The conversions were estimated on the basis of integration ratios of dialkyl/trialkyl complexes in the ^{51}V NMR spectra.[b]

vanadium(V) trialkyl complexes, V(NAr′)$(CH_2SiMe_3)_3$ (Ar′ = C_6H_5, 2-MeC_6H_4, 2,6-$Me_2C_6H_3$, 2,6-$Cl_2C_6H_3$), with 1.0 equiv of phenols (ArOH, Ar = 2,6-$F_2C_6H_3$, 2,6-$Cl_2C_6H_3$, 2,6-$Me_2C_6H_3$, 2,6-^{i}Pr$_2C_6H_3$, 2-^{t}BuC_6H_4, 2,6-^{t}Bu$_2C_6H_3$) were conducted in C_6D_6 at 25 °C, and the time profiles were monitored by ^{51}V and ^{1}H NMR spectra after addition of 1.0 equiv of ArOH (in C_6D_6, ca. 0.4 mL) into a C_6D_6 solution containing the trialkyl complex (50 μmol in ca. 0.6 mL).[b] The conversions of V(NAr′)$(CH_2SiMe_3)_3$ were estimated by the integration ratio (between the trialkyl and dialkyl complexes) in the ^{51}V NMR spectra; the ratios in the ^{1}H NMR spectra were used for confirmation (all spectra are shown in the SI).[b] In reactions using 2,6-$Cl_2C_6H_3OH$, the conversions were estimated from ^{1}H NMR spectra as a better resolution was observed.[b] The selected ^{51}V NMR spectra are summarized in Figures 1 and 2.[b]

It turned out that the reaction of V$(NC_6H_5)(CH_2SiMe_3)_3$ (Figure 1a) with 2,6-$Cl_2C_6H_3OH$ (1.0 equiv) completed within 40 min [conversion of the trialkyl complex (conv.) = 92% after 10 min (Figure 1c) and >99% after 40 min (Figure S2-2)] to afford V$(NC_6H_5)(CH_2SiMe_3)_2$(O-2,6-$Cl_2C_6H_3$) (**1b**)[b] and the reaction with 2-^{t}BuC_6H_4OH also completed within 40 min [conv. 95% after 10 min (Figure 1b), >99% after 40 min (Figure S2-5)]. The reaction with 2,6-$F_2C_6H_3OH$ completed within 10 min to afford V$(NC_6H_5)(CH_2SiMe_3)_2$(O-2,6-$F_2C_6H_3$) (**1a**, Figure S2-1).[b] In contrast, the conversions in the reaction with 2,6-$Me_2C_6H_3OH$ became slightly low [conv. 82% after 10 min (Figure 1d), and 95% after 40 min (Figures 1e and S2-3)][b] and the reaction with 2,6-^{i}Pr$_2C_6H_3OH$ proceeded slowly compared with the other phenols [conv. 34% after 10 min (Figure 1f), 61% after 40 min (Figure S2-4), 94% after 2.5 h (Figure 1g)]. Moreover, the reaction with 2,6-^{t}Bu$_2C_6H_3OH$ (3.0 equiv) at 25 °C did not take place even after 6 days (confirmed by ^{1}H and ^{51}V NMR spectra, Figure S2-22).[b] No additional new resonances in the ^{51}V NMR spectra were observed when the mixture in the reaction with 1.0 equiv of 2,6-^{t}Bu$_2C_6H_3OH$ was heated at 60 °C for 50 h after stirring at 25 °C for 4 days (no significant changes were observed upon heating in the ^{1}H NMR spectra, Figure S2-21).[b] Therefore, the substitution rates with 1.0 equiv of ArOH increased in the order: Ar = 2,6-^{t}Bu$_2C_6H_3$ ≪ 2,6-^{i}Pr$_2C_6H_3$ < 2,6-$Me_2C_6H_3$ < 2,6-$Cl_2C_6H_3$, 2-^{t}BuC_6H_4 < 2,6-$F_2C_6H_3$ (Scheme 6). Similarly, as shown in Scheme 6 (and in part in Figure 2),[b] the conversions in the reaction of V(N-2,6-$Me_2C_6H_3$)$(CH_2SiMe_3)_3$ with 1.0 equiv of ArOH increased in the order: Ar = 2,6-^{t}Bu$_2C_6H_3$ (negligible after 6 days, Figure S2-26) ≪ 2,6-^{i}Pr$_2C_6H_3$ (34% conversion after 3.5 h, Figure 2h) < 2,6-

Scheme 6. Reactions of V$(NC_6H_5)(CH_2SiMe_3)_3$ and V(N-2,6-$Me_2C_6H_3$)$(CH_2SiMe_3)_3$ with 1.0 equiv of ArOH (Ar = 2,6-$F_2C_6H_3$, 2,6-$Cl_2C_6H_3$, 2,6-$Me_2C_6H_3$, 2,6-^{i}Pr$_2C_6H_3$, 2-^{t}BuC_6H_4, 2,6-^{t}Bu$_2C_6H_3$) in C_6D_6 at 25 °C

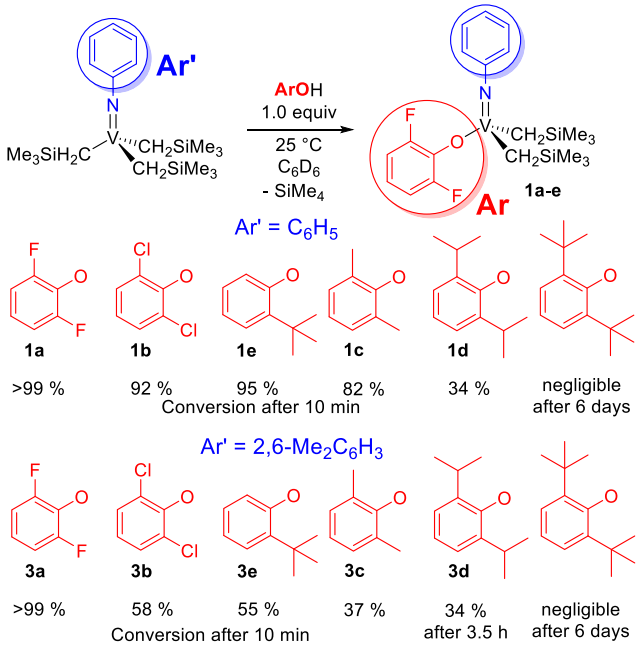

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Table 1. Reactions of $V(NAr')(CH_2SiMe_3)_3$ (Ar′ = C_6H_5, 2-MeC_6H_4, 2,6-$Me_2C_6H_3$, 2,6-$Cl_2C_6H_3$), with 1.0 equiv of Various ArOH (Ar = 2,6-$F_2C_6H_3$, 2,6-$Cl_2C_6H_3$, 2,6-$Me_2C_6H_3$, 2,6-$^iPr_2C_6H_3$, 2-$^tBuC_6H_4$, 2,6-$^tBu_2C_6H_3$) in C_6D_6 at 25 °C[a]

	conversion (%) in the reaction of $V(NAr')(CH_2SiMe_3)_3$ with ArOH[b]			
Ar′	C_6H_5	2-MeC_6H_4	2,6-$Me_2C_6H_3$	2,6-$Cl_2C_6H_3$
δ (ppm) in ^{51}V NMR[c]	1052.2	1059.4	1162.3	1076.4
2,6-$F_2C_6H_3OH$	>99% (>99%)[d]	>99% (>99%)[d]	>99% (>99%)[d]	>99% (>99%)[d]
2,6-$Cl_2C_6H_3OH$	92%[e] (≫99%)[d,e]	86%[e] (>99%)[d,e]	58%[e] (73%)[d,e]	74%[e] (87%)[d,e]
2,6-$Me_2C_6H_3OH$	82% (95%)[d]	76% (97%)[d]	37% (66%)[d]	67% (88%)[d]
2,6-$^iPr_2C_6H_3OH$	34% (61%)[d]	14% (25%)[d]	trace (8%)[d]	10% (19%)[d]
2-$^tBuC_6H_4OH$	95% (>99%)[d]	74% (89%)[d]	55% (76%)[d]	73% (86%)[d]
2,6-$^tBu_2C_6H_3OH$	negligible	negligible	negligible	negligible

[a]Conditions: $V(NAr')(CH_2SiMe_3)_3$ 50 μmol in C_6D_6 (total 1.0 mL), 25 °C. [b]Conversion (%) after 10 min estimated by the integration ratio of $V(NAr')(CH_2SiMe_3)_2(OAr)/V(NAr')(CH_2SiMe_3)_3$ by ^{51}V NMR spectra. [c]Chemical shifts (in C_6D_6) for $V(NAr')(CH_2SiMe_3)_3$ in ^{51}V NMR spectra. [d]Conversion (%) after 40 min estimated by ^{51}V NMR spectra. [e]Conversion (%) estimated by ^1H NMR spectra. Detailed data are shown in the Supporting Information.

$Me_2C_6H_3$ (37% conversion after 10 min, Figure 2g) < 2,6-$Cl_2C_6H_3$ (58% after 10 min, Figure S2-12), 2-$^tBuC_6H_4$ (55%, after 10 min, Figure S2-15) < 2,6-$F_2C_6H_3$ (>99% after 10 min, Figure 2f). These results clearly suggest that the substitution rate decreased with increasing the steric bulk in the phenolic ortho-substituents.

Table 1 summarizes the results in the reaction of $V(NAr')(CH_2SiMe_3)_3$ with ArOH (1.0 equiv) in C_6D_6 at 25 °C.[b] A similar trend shown in Scheme 6 was observed in the reaction of $V(N\text{-}2,6\text{-}Cl_2C_6H_3)(CH_2SiMe_3)_3$. Moreover, as also shown in part in Figure 2, the rates in the reaction of $V(N\text{-}2\text{-}MeC_6H_4)(CH_2SiMe_3)_3$ with ArOH (1.0 equiv) increased in the order: Ar = 2,6-$^tBu_2C_6H_3$ ≪ 2,6-$^iPr_2C_6H_3$ < 2,6-$Me_2C_6H_3$, 2-$^tBuC_6H_4$ < 2,6-$Cl_2C_6H_3$ < 2,6-$F_2C_6H_3$; the degree in the reaction with 2-$^tBuC_6H_4OH$ was close to that in the reaction with 2,6-$Me_2C_6H_3OH$.

To estimate the electronic nature in ArOH, pK_a values (in aqueous solution) in the disubstituted phenols[57−59] have been chosen, although these reactions were conducted in C_6D_6 (or *n*-hexane for isolation). It turned out that the observed orders on the substitution rates are somewhat different from the pK_a values: 2,6-$Cl_2C_6H_3OH$ (pK_a = 6.79)[57] 2,6-$F_2C_6H_3OH$ (7.58)[58] < 2,6-$Me_2C_6H_3OH$ (10.59)[57] < 2,6-$^iPr_2C_6H_3OH$ (11.1).[59] In fact, the reaction of $V(N\text{-}2,6\text{-}Me_2C_6H_3)(CH_2SiMe_3)_3$ with 1.0 equiv of PhOH (pK_a = 9.99)[57] completed within 10 min to afford $V(N\text{-}2,6\text{-}Me_2C_6H_3)(CH_2SiMe_3)_2(OPh)$[b] (data are shown in the SI, Figure S2-29).[b] It also turned out that the phenylimido complex showed higher conversions than the other arylimido complexes and the degree increased in the order: Ar′ = 2,6-$Me_2C_6H_3$ < 2,6-$Cl_2C_6H_3$ < 2-MeC_6H_4 < C_6H_5. The observed trend is somewhat different from that on the basis of chemical shifts in the ^{51}V NMR spectra, which could be related to the nucleophilic nature in the (arylimido)vanadium complexes (Table 1).[60] Taking into account these results, as described above, it is clear that the steric bulk in ArOH plays a role in the substitution rate.

CONCLUDING REMARKS

We have conducted reactions of various (arylimido)vanadium(V)−trialkyl complexes, $V(NAr')(CH_2SiMe_3)_3$ (Ar′ = C_6H_5, 2-MeC_6H_4, 2,6-$Me_2C_6H_3$, 2,6-$Cl_2C_6H_3$), with 1.0 equiv of phenols (ArOH, Ar = 2,6-$F_2C_6H_3$, 2,6-$Cl_2C_6H_3$, 2,6-$Me_2C_6H_3$, 2,6-$^iPr_2C_6H_3$, 2-$^tBuC_6H_4$, 2,6-$^tBu_2C_6H_3$) in C_6D_6 at 25 °C and explored effects of both arylimido ligand and phenol on the substitution rate. The phenylimido complex showed the highest conversions, and the degree increased in the order: Ar′ = 2,6-$Me_2C_6H_3$ < 2,6-$Cl_2C_6H_3$ < 2-MeC_6H_4 < C_6H_5. The order is somewhat different from that obtained from the chemical shifts in $V(NAr')(CH_2SiMe_3)_3$ in the ^{51}V NMR spectra. Moreover, conversions in the reaction of $V(NAr')(CH_2SiMe_3)_3$ with disubstituted phenols increased in the order: 2,6-$^iPr_2C_6H_3OH$ < 2,6-$Me_2C_6H_3OH$ < 2,6-$Cl_2C_6H_3OH$ < 2,6-$F_2C_6H_3OH$, irrespective of the kind of the arylimido ligands employed. The order is also somewhat different from that of pK_a values (employed for estimation of the electronic nature), and the reactions of $V(NAr')(CH_2SiMe_3)_3$ with 1.0 (and 3.0) equiv of 2,6-$^tBu_2C_6H_3OH$ did not take place even upon heating at 60 °C.[56] Taking into account these results, it is highly suggested that, as proposed previously,[42,48−50] the reactions proceeded by coordination of phenols into the vanadium metal center. Through this study, it is clear that steric bulk in both arylimido and phenol affects the substitution rate. We highly believe that the results should be promising and should be useful for better understanding, especially in the field of organometallic chemistry of vanadium.

EXPERIMENTAL SECTION

General Procedures. All experiments were performed under a nitrogen atmosphere in a vacuum atmosphere (VAC) drybox. Anhydrous grade *n*-hexane, tetrahydrofuran, and dichloromethane (Kanto Chemical Co., Inc.) and *n*-octane (Aldrich) were stored in a bottle containing molecular sieves (a mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox and were passed through a short alumina column under a N_2 stream prior to use. The other reagents (phenols) of reagent grade were dried in the presence of molecular sieves and alumina passed through a short column prior to use. $V(NPh)Cl_3$,[61] $V(N\text{-}2\text{-}MeC_6H_4)Cl_3$,[62] $V(N\text{-}2,6\text{-}Me_2C_6H_3)Cl_3$,[63] $V(NPh)(CH_2SiMe_3)_3$,[54] $V(N\text{-}2,6\text{-}Me_2C_6H_3)(CH_2SiMe_3)_3$,[48] $V(N\text{-}2,6\text{-}Me_2C_6H_3)(CH_2SiMe_3)_2(O\text{-}2,6\text{-}F_2C_6H_3)$ (**3a**),[49] $V(N\text{-}2,6\text{-}Me_2C_6H_3)(CH_2SiMe_3)_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**3c**),[48] $V(N\text{-}2,6\text{-}Me_2C_6H_3)(CH_2SiMe_3)_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**3d**),[48] and $V(N\text{-}2,6\text{-}Me_2C_6H_3)(CH_2SiMe_3)_2(OC_6H_5)$[48] were prepared according to the previous reports.

All NMR spectra were recorded on a Bruker AV500 spectrometer (500.13 MHz for ^1H, 125.77 MHz for ^{13}C, 470.59 MHz for ^{19}F, 202.47 MHz for ^{31}P, 131.55 MHz for ^{51}V) unless otherwise noted. All spectra were obtained at 25 °C unless otherwise noted. Chemical shifts are given in ppm and are referenced to $SiMe_4$ (δ 0.00, ^1H, ^{13}C), $CFCl_3$ (δ 0.00, ^{19}F) and $VOCl_3$ (δ 0.00, ^{51}V). Coupling constants and half-width values, $\Delta\nu_{1/2}$, are given in hertz. Elemental analyses were performed by

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using an EAI CE-440 CHN/O/S Elemental Analyzer (Exeter Analytical, Inc.).

*Synthesis of V(NPh)(CH_2SiMe_3)$_2$(O-2,6-$F_2C_6H_3$) (**1a**).* Into an *n*-hexane solution (30 mL) containing V(NPh)(CH_2SiMe_3)$_3$ (407 mg, 1.01 mmol) was added 2,6-$F_2C_6H_3OH$ (156 mg, 1.20 mmol) at −30 °C. The solution was stirred at room temperature for 5 h, and the completion of consumption of 2,6-$F_2C_6H_3OH$ was confirmed by ^{1}H NMR spectrum. The resultant solution was filtered through a celite pad; the filter cake was washed with *n*-hexane. The filtrate and the wash liquid were placed into a rotary evaporator combined to remove volatiles, affording a sticky brown liquid. Yield: 237 mg (87%). ^{1}H NMR (C_6D_6): δ 0.13 (s, 18H, CH_2SiMe_3), 2.37 (s, 2H, CH_2SiMe_3), 2.91 (br, 2H, CH_2SiMe_3), 6.21 (br, 1H, Ar-*H*), 6.51 (br, 2H, Ar-*H*), 6.80 (t, 1H, *J* = 7.4, Ar-*H*), 7.02 (t, 2H, *J* = 7.5, Ar-*H*), 7.51 (d, 2H, *J* = 7.8, Ar-*H*). ^{51}V NMR (C_6D_6): δ 577 ($\Delta\nu_{1/2}$ = 314 Hz). ^{19}F NMR (C_6D_6): δ −129.0 (s). ^{13}C NMR (C_6D_6): δ 1.7 ($SiMe_3$), 90.3−94.4 (br, V-CH_2), 111.6, 120.3, 125.5, 126.2, 128.7, 153.0, 154.9, 166.0 (Ar). Anal. calcd for $C_{20}H_{30}F_2NOSi_2V$: C, 53.91; H, 6.79; N, 3.14. Found: C, 53.86; H, 6.75; N, 3.13.

*Synthesis of V(NPh)(CH_2SiMe_3)$_2$(O-2,6-$Cl_2C_6H_3$) (**1b**).* Synthesis of **1b** was carried out by the same procedure as that for **1a** except that V(NPh)(CH_2SiMe_3)$_3$ (288 mg, 0.713 mmol) was used and 2,6-$Cl_2C_6H_3OH$ (116 mg, 0.712 mmol) was added in the place of 2,6-$F_2C_6H_3OH$. Yield: 336 mg (99%). ^{1}H NMR (C_6D_6): δ 0.15 (s, 18H, CH_2SiMe_3), 2.34 (br, 2H, CH_2SiMe_3), 3.15 (br, 2H, CH_2SiMe_3), 6.20 (t, 1H, *J* = 8.0, Ar-*H*), 6.81 (t, 1H, *J* = 7.3, Ar-*H*), 6.93 (d, 2H, *J* = 8.1, Ar-*H*), 7.03 (t, 2H, *J* = 7.6, Ar-*H*), 7.52 (d, 2H, *J* = 7.8, Ar-*H*). ^{51}V NMR (C_6D_6): δ 500 ($\Delta\nu_{1/2}$ = 309 Hz). ^{13}C NMR (C_6D_6): δ 1.87 ($SiMe_3$), 95.0 (br, V-CH_2), 118.6, 120.9, 121.8, 125.1, 125.5, 125.8, 126.2, 156.6, 165.3 (Ar). Anal. calcd for $C_{20}H_{30}Cl_2NOSiV$: C, 50.20, H, 6.32, N, 2.93. Found: 49.69, H, 6.13, N, 3.02. The observed C values was somewhat low, probably due to incomplete combustion (by production of vanadium carbide), whereas both H and N observed value were close to the calculated values.

*Synthesis of V(NPh)(CH_2SiMe_3)$_2$(O-2,6-$Me_2C_6H_3$) (**1c**).* Synthesis of **1c** was carried out by the same procedure as that for **1a** except that V(NPh)(CH_2SiMe_3)$_3$ (400 mg, 0.991 mmol) was used and 2,6-$Me_2C_6H_3OH$ (122 mg, 1.00 mmol) was added in the place of 2,6-$F_2C_6H_3OH$. Yield: 258 mg (99%). ^{1}H NMR (C_6D_6): δ 0.14 (s, 18H, CH_2SiMe_3), 2.15 (br, 2H, CH_2SiMe_3), 2.34 (s, 6H, Ar-*Me*), 2.66 (br, 2H, CH_2SiMe_3), 6.78 (m, 2H, Ar-*H*), 6.93 (d, 2H, *J* = 7.4, Ar-*H*), 7.01 (t, 2H, *J* = 7.6, Ar-*H*), 7.37 (d, 2H, *J* = 7.9, Ar-*H*). ^{51}V NMR (C6D$_6$): δ 508 ($\Delta\nu_{1/2}$ = 385 Hz). ^{13}C NMR (C_6D_6): δ 2.03 ($SiMe_3$), 17.7 (2,6-$Me_2C_6H_3$), 85.5−90.9 (br, V-CH_2), 120.2, 122.5, 122.6, 125.4, 125.8, 126.2, 127.0, 128.7, 128.8, 129.1, 164.8 (Ar). Anal. calcd for $C_{22}H_{36}NOSi_2V$: C, 60.38; H, 8.29; N, 3.20. Found: C, 60.28; H, 8.10; N, 3.29.

*Synthesis of V(NPh)(CH_2SiMe_3)$_2$(O-2,6-^{i}Pr$_2C_6H_3$) (**1d**).* Synthesis of **1d** was carried out by the same procedure as that for **1a** except that V(NPh)(CH_2SiMe_3)$_3$ (412 mg, 1.02 mmol) was used and 2,6-^{i}Pr$_2C_6H_3OH$ (179 mg, 1.01 mmol) was added in the place of 2,6-$F_2C_6H_3OH$. Yield: 487 mg (98%). ^{1}H NMR (C_6D_6): δ 0.16 (s, 18H, CH_2SiMe_3), 1.26 (d, 12H, *J* = 6.9, ^{i}*Pr*), 2.10 (d, 2H, *J* = 9.4, CH_2SiMe_3), 2.86 (d, 2H, *J* = 9.6, CH_2SiMe_3), 3.73 (sep, 2H, *J* = 6.9, ^{i}*Pr*), 6.79 (t, 1H, *J* = 7.43, Ar-*H*), 6.96 (t, 1H, *J* = 7.6, Ar-*H*), 7.02 (t, 2H, *J* = 7.9, Ar-*H*), 7.06 (d, 2H, *J* = 7.6, Ar-*H*), 7.42 (d, 2H, *J* = 7.7, Ar-*H*). ^{51}V NMR (C_6D_6): δ 500 ($\Delta\nu_{1/2}$ = 323 Hz). ^{13}C NMR (C_6D_6): δ 2.1 ($SiMe_3$), 23.6 (Me_2CH−), 27.1 (Me_2CH−), 88.2 (br, V-CH_2), 120.2, 123.3, 123.4, 125.3, 125.7, 126.3, 128.7, 128.9, 137.7, 137.9, 160.7, 164.2 (Ar). Anal. calcd for $C_{26}H_{44}NOSi_2V$: C, 63.25; H, 8.98; N, 2.84. Found: C, 62.97; H, 9.16; N, 2.96.

*Synthesis of V(NPh)(CH_2SiMe_3)$_2$(O-2-^{t}BuC_6H_4) (**1e**).* Synthesis of **1e** was carried out by the same procedure as that for **1a** except that V(NPh)(CH_2SiMe_3)$_3$ (402 mg, 0.996 mmol) was used and 2-^{t}BuC_6H_4OH (150 mg, 1.00 mmol) was added in the place of 2,6-$F_2C_6H_3OH$. Yield: 461 mg (99%).^{1}H NMR (C_6D_6): δ 0.11 (s, 18H, CH_2SiMe_3), 1.70 (s, 9H, ^{t}*Bu*), 2.07 (br, 2H, CH_2SiMe_3), 2.79 (br, 2H, CH_2SiMe_3), 6.82 (m, 2H, Ar-*H*), 6.91 (dt, 1H, $^3J_{H-H}$ = 8.0, $^4J_{H-H}$ = 1.4, Ar-*H*), 7.05 (t, 2H, *J* = 7.8, Ar-*H*), 7.21 (d, 1H, $^3J_{H-H}$ = 8.0, Ar-*H*), 7.25 (dd, 1H, $^3J_{H-H}$ = 7.8, $^4J_{H-H}$ = 1.4, Ar-*H*), 7.55 (d, 2H, *J* = 7.7, Ar-*H*). ^{51}V NMR (C_6D_6): δ 500 ($\Delta\nu_{1/2}$ = 312 Hz). ^{13}C NMR (C_6D_6): δ 2.2 ($SiMe_3$), 30.5 (Me_3C−), 35.2 (Me_3C−), 86.2−89.8 (br, V-CH_2), 119.8, 123.3, 125.5, 125.9, 126.8, 127.6, 128.9, 129.3, 135.5, 162.9 (Ar). Anal. calcd for $C_{24}H_{40}NOSi_2V$: C, 61.90; H, 8.66; N, 3.01. Found: C, 62.15; H, 8.83; N, 2.97.

Synthesis of V(N-2-MeC_6H_4)(CH_2SiMe_3)$_3$. Into an tetrahydrofuran solution (60 mL) containing LiCH_2SiMe_3 (1.96 g, 20.8 mmol) was added V(N-2-MeC_6H_4)Cl_3 (1.78 g, 6.78 mmol) at −30 °C. The solution was stirred at room temperature for 3 h. The resultant solution was filtered through a Celite Pad, the filter cake was washed with *n*-hexane. Combined, the filtrate and the wash liquid were placed into a rotary evaporator to remove volatiles, affording a sticky brown liquid. Yield: 1.84 g (65%). ^{1}H NMR (C_6D_6): δ 0.13 (s, 24H, CH_2SiMe_3), 1.88 (br, 6H, CH_2SiMe_3), 2.71 (s, 3H, Ar-*Me*), 6.84 (t, 1H, *J* = 7.4, Ar-*H*), 7.05 (m, 2H, Ar-*H*), 7.72 (d, 1H, *J* = 7.8, Ar-*H*). ^{51}V NMR (C_6D_6): δ 1059. ^{13}C NMR (C_6D_6): δ 2.2 ($SiMe_3$), 19.7 (2-*Me*C_6H_4), 87.1−90.6 (br, V-CH_2), 125.4, 126.3, 126.6, 130.5, 133.3 164.8 (Ar). Several attempts for analysis failed due to its appearing very sensitive (probably toward impurities, including even a trace amount of moisture and oxygen).

*Synthesis of V(N-2-MeC_6H_4)(CH_2SiMe_3)$_2$(O-2,6-$F_2C_6H_3$) (**2a**).* Into an *n*-hexane solution (30 mL) containing V(N-2-MeC_6H_4)(CH_2SiMe_3)$_3$ (202 mg, 0.484 mmol) was added 2,6-$F_2C_6H_3OH$ (70 mg, 0.538 mmol) at −30 °C. The solution was stirred at room temperature for 5 h, and completion of consumption of 2,6-$F_2C_6H_3OH$ was confirmed by ^{1}H NMR spectrum. The resultant solution was filtered through a celite pad and the filter cake was washed with *n*-hexane. Combined, the filtrate and the wash liquid were placed into a rotary evaporator to remove volatiles, affording a sticky brown liquid. Yield: 194 mg (87%). ^{1}H NMR (C_6D_6): δ 0.14 (s, 18H, CH_2SiMe_3), 2.44 (br, 2H, CH_2SiMe_3), 2.54 (s, 3H, Ar-*Me*), 2.86 (br, 2H, CH_2SiMe_3), 6.23 (m, 1H, Ar-*H*), 6.52 (t, 2H, *J* = 7.7, Ar-*H*), 6.76 (t, 1H, *J* = 7.4, Ar-*H*), 6.93 (m, 2H, Ar-*H*), 7.57 (d, 1H, *J* = 7.8, Ar-*H*). ^{51}V NMR (C_6D_6): δ 595 ($\Delta\nu_{1/2}$ = 320 Hz). ^{19}F NMR (C_6D_6): δ −128.7 (t, $^4J_{F-F}$ = 6.6). ^{13}C NMR (C_6D_6): δ 1.6 ($SiMe_3$), 18.8 (2-*Me*C_6H_4), 95.6 (br, V-CH_2), 111.4 (dd, $^2J_{C-F}$ =16.4, $^4J_{C-F}$ = 5.9), 120.0 (t, $^3J_{C-F}$ = 8.8), 126.3, 126.3, 127.1, 130.2, 134.3 (Ar), 153.7 (dd, $^1J_{C-F}$ = 247, $^3J_{C-F}$ = 4.7), 161.0 (Ar). Anal. calcd for $C_{21}H_{32}F_2NOSi_2V$: C, 54.88; H, 7.02; N, 3.05. Found(1): C, 54.21; H, 6.76; N, 3.12. Found(2): C, 54.52; H, 6.83; N, 3.34. The observed C values were somewhat low because of the incomplete combustion (by production of vanadium carbide), whereas both H and N observed values were close to the calculated values.

*Synthesis of V(N-2-MeC_6H_4)(CH_2SiMe_3)$_2$(O-2,6-$Cl_2C_6H_3$) (**2b**).* Synthesis of **2b** was carried out by the same procedure as that for **2a** except that V(N-2-MeC_6H_4)(CH_2SiMe_3)$_3$ (217 mg, 0.519 mmol) was used and 2,6-$Cl_2C_6H_3OH$ (108 mg, 0.662

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mmol) was added in the place of 2,6-$F_2C_6H_3OH$. Yield: 233 mg (91%). ^{1}H NMR (C_6D_6): δ 0.14 (s, 18H, CH_2SiMe_3), 2.45 (d, 2H, J = 7.6, CH_2SiMe_3) 2.56 (s, 3H, Ar-*Me*), 2.99 (d, 2H, J = 7.2, CH_2SiMe_3), 6.20 (t, 1H, J = 8.0, Ar-*H*), 6.77 (m, 1H, Ar-*H*), 6.93 (m, 4H, Ar-*H*), 7.57 (d, 1H, J = 7.8, Ar-*H*). ^{51}V NMR (C_6D_6): δ 619 ($\Delta\nu_{1/2}$ = 325 Hz). ^{13}C NMR (C_6D_6): δ 1.8 ($SiMe_3$), 18.9 (2-*Me*C_6H_4), 91.1−95.5 (br, V-CH_2), 121.9, 125.6, 126.3, 126.3, 127.5, 128.4, 130.3, 134.4, 157.1, 159.3 (Ar). Anal. calcd for $C_{21}H_{32}Cl_2NOSi_2V$: C, 51.21; H, 6.55; N, 2.84. Found: C, 50.97; H, 6.66; N, 2.73.

*Synthesis of V(N-2-MeC$_6$H$_4$)(CH$_2$SiMe$_3$)$_2$(O-2,6-Me$_2$C$_6$H$_3$) (**2c**).* Synthesis of **2c** was carried out by the same procedure as that for **2a** except that V(N-2-MeC_6H_4)(CH_2SiMe_3)$_3$ (302 mg, 0.723 mmol) was used and 2,6-$Me_2C_6H_3OH$ (88 mg, 0.720 mmol) was added in the place of 2,6-$F_2C_6H_3OH$. Yield: 310 mg (95%). ^{1}H NMR (C_6D_6): δ 0.16 (s, 18H, CH_2SiMe_3), 2.29 (m, 8H, Ar-*Me* and CH_2SiMe_3) 2.40 (d, 2H, J = 7.2, CH_2SiMe_3), 2.47 (s, 3H, Ar-*Me*), 6.76−6.79 (m, 2H, Ar-*H*), 6.89−6.93 (m, 4H, Ar-*H*), 7.38 (d, 1H, J = 7.6, Ar-*H*). ^{51}V NMR (C_6D_6): δ 512 ($\Delta\nu_{1/2}$ = 352 Hz). ^{13}C NMR (C_6D_6): δ 2.0 ($SiMe_3$), 19.1 (2-*Me*C_6H_4), 30.4 (Me_2CH−), 35.2 (Me_2CH−), 123.3, 123.4, 126.0, 126.4, 126.7, 126.5, 127.5, 130.5, 134.2, 135.6, 152.8 (Ar). Anal. calcd for $C_{23}H_{38}NOVSi_2V$: C, 61.16, H, 8.48, N, 3.10. Found(1): C, 60.57, H, 8.33, N, 3.44. Found(2): C, 60.5, H, 8.05, N, 3.4. The observed *C* values were somewhat low because of the incomplete combustion (by production of vanadium carbide), whereas both H and N observed values were close to the calculated values.

*Synthesis of V(N-2-MeC$_6$H$_4$)(CH$_2$SiMe$_3$)$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**2d**).* Synthesis of **2d** was carried out by the same procedure as that for **2a** except that V(N-2-MeC_6H_4)(CH_2SiMe_3)$_3$ (303 mg, 0.725 mmol) was used and 2,6-^{i}Pr$_2C_6H_3OH$ (130 mg, 0.729 mmol) was added in the place of 2,6-$F_2C_6H_3OH$ and the reaction mixture was stirred overnight. Yield: 359 mg (98%). ^{1}H NMR (C_6D_6): δ 0.18 (s, 18H, CH_2SiMe_3), 1.23 (d, 12H, J = 6.9, ^{i}*Pr*) 2.19 (d, 2H, J = 10.5, CH_2SiMe_3), 2.45 (s, 3H, Ar-*Me*), 2.56 (d, 2H, J = 10.5, CH_2SiMe_3), 3.61 (sep, 2H, J = 6.9, ^{i}*Pr*), 6.74 (t, 1H, J = 7.4, Ar-*H*), 6.98−6.96 (m, 3H, Ar-*H*), 7.04 (d, 2H, J = 7.5, Ar-*H*), 7.44 (d, 1H, J = 7.7, Ar-*H*). ^{51}V NMR (C_6D_6): δ 519 ($\Delta\nu_{1/2}$ = 400 Hz). ^{13}C NMR (C_6D_6): δ 2.0 ($SiMe_3$), 18.9 (2-*Me*C_6H_4), 23.6 (Me_2CH−), 27.0 (Me_2CH−), 123.3, 123.5, 125.9, 126.5, 134.1, 137.4, 137.6, 150.5, 159.8 (Ar). Anal. calcd for $C_{27}H_{46}NOSi_2V$: C, 63.86; H, 9.13; N, 2.76. Found: C, 63.63; H, 9.35; N, 2.80.

*Synthesis of V(N-2-MeC$_6$H$_4$)(CH$_2$SiMe$_3$)$_2$(O-2-^{t}BuC$_6$H$_4$) (**2e**).* Synthesis of **2e** was carried out by the same procedure as that for **2a** except that V(N-2-MeC_6H_4)(CH_2SiMe_3)$_3$ (307 mg, 0.735 mmol) was used and 2-^{t}BuC$_6$H$_4$OH (112 mg, 0.746 mmol) was added in the place of 2,6-$F_2C_6H_3OH$. Yield: 324 mg (92%). ^{1}H NMR (C_6D_6): δ 0.10 (s, 18H, CH_2SiMe_3), 1.70 (s, 9H, ^{t}*Bu*), 2.25 (br, 2H, CH_2SiMe_3), 2.60 (s, 3H, Ar-*Me*), 2.68 (br, 2H, CH_2SiMe_3), 6.79−6.87 (m, 2H, Ar-*H*), 6.87 (t, 1H, J = 7.2, Ar-*H*), 6.95−7.00 (m, 2H, Ar-*H*), 7.09 (d, 1H, J = 7.8, Ar-*H*), 7.25 (d, 1H, J = 7.5, Ar-*H*), 7.61 (d, 1H, J = 7.8, Ar-*H*). ^{51}V NMR (C_6D_6): δ 509 ($\Delta\nu_{1/2}$ = 320 Hz). ^{13}C NMR (in C_6D_6): δ 1.7 ($SiMe_3$), 18.8 (2-*Me*C_6H_4), 30.1 (Me_3C−), 34.9 (Me_3C−), 122.9, 123.1, 125.7, 126.1, 126.2, 126.4, 127.2, 130.2, 133.9, 135.3, 162.8 (Ar). Anal. calcd for $C_{25}H_{42}NOSi_2V$: C, 62.59; H, 8.82; N, 2.92. Found(1): C, 61.45; H, 8.62; N, 2.96. Found(2): C, 60.99; H, 8.59; N, 3.03. The observed C values were somewhat low because of the incomplete combustion (by production of vanadium carbide), whereas both H and N observed values were close to the calculated values.

*Synthesis of V(N-2,6-Me$_2$C$_6$H$_3$)(CH$_2$SiMe$_3$)$_2$(O-2,6-Cl$_2$C$_6$H$_3$) (**3b**).* Into an *n*-hexane solution (30 mL) containing V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_3$ (326 mg, 0.755 mmol) was added 2,6-$Cl_2C_6H_3OH$ (133 mg, 0.816 mmol) at −30 °C. The solution was stirred at room temperature for 5 h. The resultant solution was placed into a rotary evaporator to remove volatiles, affording a sticky brown liquid. Yield: 380 mg (99%). ^{1}H NMR (C_6D_6): δ 0.20 (s, 18H, CH_2SiMe_3), 2.45 (d, 2H, J = 10.5, CH_2SiMe_3), 2.53 (s, 6H, Ar-Me_2), 2.83 (d, 2H, J = 10.9, CH_2SiMe_3), 6.18 (t, 1H, J = 8.1, Ar-*H*), 6.70 (t, 1H, J = 7.5, Ar-*H*), 6.81 (d, 2H, J = 7.5, Ar-*H*), 6.88 (d, 2H, J = 8.1, Ar-*H*). ^{51}V NMR (C_6D_6): δ 633 ($\Delta\nu_{1/2}$ = 400 Hz). ^{13}C NMR (C_6D_6): δ 1.7 ($SiMe_3$), 19.3 (Ar-*Me*), 121.9, 125.6, 126.1, 127.9, 128.4, 129.7, 130.0, 135.9, 157.3, 157.8 (Ar).

*Synthesis of V(N-2,6-Me$_2$C$_6$H$_3$)(CH$_2$SiMe$_3$)$_2$(O-2-^{t}BuC$_6$H$_4$) (**3e**).* Synthesis of **3e** was carried out by the same procedure as that for **3b** except that V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_3$ (349 mg, 0.808 mmol) was used and 2,6-^{t}BuC$_6$H$_4$OH (118 mg, 0.786 mmol) was added in the place of 2,6-$Cl_2C_6H_3OH$. Yield: 387 mg (99%). ^{1}H NMR (C_6D_6): δ 0.13 (s, 18H, CH_2SiMe_3), 1.64 (s, 9H, ^{t}*Bu*), 2.17 (br, 2H, CH_2SiMe_3), 2.56 (s, 6H, Ar-*Me*), 2.75 (br, 2H, CH_2SiMe_3), 6.72−6.77 (m, 3H, Ar-*H*), 6.82 (d, 1H, J = 7.9, Ar-*H*), 6.85 (d, 2H, J = 7.5, Ar-*H*), 7.20 (d, 1H, J = 7.4, Ar-*H*). ^{51}V NMR (C_6D_6): δ 518 ($\Delta\nu_{1/2}$ = 385 Hz). ^{13}C NMR (C_6D_6): δ 2.0 ($SiMe_3$), 19.4 (Ar-*Me*), 30.3 (Me_3C−), 35.1 (Me_3C−), 123.2, 123.7, 125.7, 126.6, 127.4, 129.0, 135.2, 135.7, 163.6 (Ar). Anal. calcd for $C_{26}H_{44}NOSi_2V$: C, 63.25; H, 8.98; N, 2.84. Found: C, 63.05; H, 8.88; N, 2.95.

Synthesis of V(N-2,6-Cl$_2$C$_6$H$_3$)Cl$_3$. $VOCl_3$ (4.18 g, 24.1 mmol) was added into a *n*-octane (50 mL) solution containing 2,6-dichlorophenyl isocyanate (2.73 g, 14.5 mmol) in a sealed Schlenk tube in the drybox. After washing the tube with *n*-octane (5 mL), the mixture was heated in an oil bath at 140 °C and the mixture was stirred overnight (17 h). During the reaction especially at the beginning, the CO_2 by-product was carefully removed from the mixture through a nitrogen line. After the reaction, the mixture was cooled at room temperature and was filtered through a celite pad. The filter cake was washed with *n*-hexane to extract VCl_3(*N*-2,6-$Cl_2C_6H_3$). Combined, the filtrate and wash liquid were added to toluene and placed in vacuo to remove volatiles. The resultant solid was dissolved in a minimum amount of dichloromethane, and the chilled solution (−30 °C) afforded a deep green solid (4.43 g, 14.0 mmol). Yield: 97% (based on 2,6-dichlorophenyl isocyanate). ^{1}H NMR (C_6D_6): δ 5.79 (t, 1H, J = 7.5, Ar-H), 6.27 (d, 2H, J = 7.5, Ar-H). ^{51}V NMR (C_6D_6): δ 262 ($\Delta\nu_{1/2}$ = 354 Hz). ^{13}C NMR (C_6D_6): δ 127.6, 131.2, 135.4, 165.6. Anal. calcd for $C_6H_3Cl_5NV$: C, 22.71; H, 0.95; N, 4.41. Found: C, 23.01; H, 0.91; N, 4.50.

Synthesis of V(N-2,6-Cl$_2$C$_6$H$_3$)(CH$_2$SiMe$_3$)$_3$. Into a tetrahydrofuran solution (60 mL) containing $LiCH_2SiMe_3$ (2.08 g, 22.1 mmol) was added V(N-2,6-$Cl_2C_6H_3$)Cl_3 (2.27 mg, 7.16 mmol) at −30 °C. The solution was stirred at room temperature for 3 h. The resultant solution was filtered through a celite pad and the filter cake was washed with *n*-hexane. Combined, the filtrate and the wash liquid were placed into a rotary evaporator to remove volatiles, affording a sticky brown liquid. Yield: 2.35 mg (70%). ^{1}H NMR (C_6D_6): δ 0.17 (s, 18H, CH_2SiMe_3), 2.22 (br, 6H, CH_2SiMe_3), 6.22 (t, 1H, J = 8.0, Ar-*H*), 6.97 (d, 1H, J = 8.1, Ar-*H*). ^{51}V NMR (C_6D_6): δ 1162. ^{13}C NMR (C_6D_6): δ 2.36 ($SiMe_3$), 93.0−96.8 (br, V-CH_2), 124.7, 125.1, 126.6, 128.5, 131.9, 158.6 (Ar). Anal. calcd for $C_{18}H_{36}Cl_2NOSi_3V$: C, 45.75; H, 7.68; N, 2.96. Found: C, 45.53; H, 7.52; N, 2.86.

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*Synthesis of V(N-2,6-$Cl_2C_6H_3$)(CH_2SiMe_3)$_2$(O-2,6-$F_2C_6H_3$) (**4a**).* Into an *n*-hexane solution (30 mL) containing V(N-2,6-$Cl_2C_6H_3$)(CH_2SiMe_3)$_3$ (300 mg, 0.635 mmol) was added 2,6-$F_2C_6H_3OH$ (97 mg, 0.746 mmol) at −30 °C. The solution was warmed slowly to room temperature (total 5 h). The resultant mixture was placed into a rotary evaporator to remove volatiles to afford a sticky brown liquid. Yield: 272 mg (83%). ^{1}H NMR (C_6D_6): δ 0.19 (s, 18H, CH_2SiMe_3), 2.93 (br, 2H, CH_2SiMe_3), 3.14 (br, 2H, CH_2SiMe_3), 6.14 (t, 1H, J = 8.1, Ar-*H*), 6.25 (m, 1H, Ar-*H*), 6.52 (t, 2H, J = 7.8, Ar-*H*), 6.82 (d, 2H, J = 8.1, Ar-*H*). ^{51}V NMR (C_6D_6): δ 657 ($\Delta\nu_{1/2}$ = 287 Hz). ^{13}C NMR (C_6D_6): δ 1.4 ($SiMe_3$), 111.6 (dd, $^2J_{C-F}$ = 16.7, $^4J_{C-F}$ = 5.7), 120.2 (t, $^3J_{C-F}$ = 8.9), 125.6, 132.6, 154.1 (dd, $^1J_{C-F}$ = 247, $^3J_{C-F}$ = 4.6), 164.2 (Ar). ^{19}F NMR (C_6D_6): δ −127.5 (t, $^4J_{F-F}$ = 6.6, Ar-F). Anal. calcd for $C_{20}H_{28}Cl_2F_2NOSi_2V$: C, 46.69; H, 5.49; N, 2.72. Found: C, 46.39; H, 5.47; N, 2.86.

*Synthesis of V(N-2,6-$Cl_2C_6H_3$)(CH_2SiMe_3)$_2$(O-2,6-$Cl_2C_6H_3$) (**4b**).* Synthesis of **4b** was carried out by the same procedure as that for **4a** except that V(N-2,6-$Cl_2C_6H_3$)(CH_2SiMe_3)$_3$ (248 mg, 0.525 mmol) was used and 2,6-$Cl_2C_6H_3OH$ (84 mg, 0.515 mmol) was added in the place of 2,6-$F_2C_6H_3OH$. Yield: 260 mg (91%). ^{1}H NMR (C_6D_6): δ 0.22 (s, 18H, CH_2SiMe_3), 2.87 (br, 2H, CH_2SiMe_3), 3.19 (br, 2H, CH_2SiMe_3), 6.13 (t, 1H, J = 8.0, Ar-*H*), 6.19 (t, 1H, J = 8.0, Ar-*H*), 6.82 (d, 2H, J = 8.0, Ar-*H*), 6.89 (d, 2H, J = 8.0, Ar-*H*). ^{51}V NMR (C_6D_6): δ 675 ($\Delta\nu_{1/2}$ = 487 Hz). ^{13}C NMR (C_6D_6): δ 1.6 ($SiMe_3$), 98.5−100.9 (br, V-CH_2), 122.3, 125.6, 126.0, 128.0, 128.3, 132.8, 144.7, 148.1, 157.4 (Ar). Anal. calcd for $C_{20}H_{28}Cl_4NOSi_2V$: C, 43.98; H, 5.16; N, 2.56. Found: C, 44.05; H, 5.04; N, 2.60.

*Synthesis of V(N-2,6-$Cl_2C_6H_3$)(CH_2SiMe_3)$_2$(O-2,6-$Me_2C_6H_3$) (**4c**).* Synthesis of **4c** was carried out by the same procedure as that for **4a** except that V(N-2,6-$Me_2C_6H_3$)(CH_2SiMe_3)$_3$ (236 mg, 0.499 mmol) was used and 2,6-$Cl_2C_6H_3OH$ (69 mg, 0.565 mmol) was added in the place of 2,6-$F_2C_6H_3OH$. Yield: 248 mg (98%). ^{1}H NMR (C_6D_6): δ 0.20 (s, 18H, CH_2SiMe_3), 2.28 (s, 6H, Ar-*Me*), 2.40 (br, 2H, CH_2SiMe_3), 2.94 (br, 2H, CH_2SiMe_3), 6.14 (t, 1H, J = 8.1, Ar-*H*), 6.77 (t, 1H, J = 7.5, Ar-*H*), 6.83 (d, 2H, J = 8.1, Ar-*H*), 6.90 (d, 2H, J = 7.4, Ar-*H*). ^{51}V NMR (C_6D_6): δ 577 ($\Delta\nu_{1/2}$ = 342 Hz). ^{13}C NMR (C_6D_6): δ 1.7 ($SiMe_3$), 17.6 (Ar-*Me*), 122.8, 125.2, 127.4, 127.9, 128.3, 128.6, 132.4, 164.2 (Ar). Anal. calcd for $C_{22}H_{34}Cl_2NOSi_2V$: C, 52.17; H, 6.77; N, 2.77. Found (1): C, 51.78; H, 6.71; N, 2.71. Found(2): C, 51.64; H, 6.51; N, 2.64. The observed C values were somewhat low because of the incomplete combustion (by production of vanadium carbide), whereas both H and N observed values were close to the calculated values.

*Synthesis of V(N-2,6-$Cl_2C_6H_3$)(CH_2SiMe_3)$_2$(O-2,6-$^iPr_2C_6H_3$) (**4d**).* Synthesis of **4d** was carried out by the same procedure as that for **4a** except that V(N-2,6-$Cl_2C_6H_3$)(CH_2SiMe_3)$_3$ (237 mg, 0.549 mmol) was used and 2,6-$^iPr_2C_6H_3OH$ (109 mg, 0.611 mmol) was added in the place of 2,6-$F_2C_6H_3OH$ and the mixture was stirred overnight. Yield: 278 mg (90%). ^{1}H NMR (C_6D_6): δ 0.26 (s, 18H, CH_2SiMe_3), 1.21 (d, 12H, J = 6.9, ^iPr), 2.45 (d, 2H, J = 10.4, CH_2SiMe_3), 2.86 (d, 2H, J = 10.2, CH_2SiMe_3), 3.52 (sep, 2H, J = 6.8, ^iPr), 6.13 (t, 1H, J = 8.1, Ar-*H*), 6.81 (d, 2H, J = 8.1, Ar-*H*), 6.95 (t, 1H, J = 7.6, Ar-*H*), 7.03 (d, 2H, J = 7.6, Ar-*H*). ^{51}V NMR (C_6D_6): δ 577 ($\Delta\nu_{1/2}$ = 362 Hz). ^{13}C NMR (C_6D_6): δ 1.8 ($SiMe_3$), 23.6 (Me_2CH−), 27.1 (Me_2CH−), 123.5, 123.7, 125.2, 132.3, 137.8, 162.3 (Ar). Sample for the crystallographic analysis was obtained upon recrystallization.

*Synthesis of V(N-2,6-$Cl_2C_6H_3$)(CH_2SiMe_3)$_2$(O-2-$^tBuC_6H_4$) (**4e**).* Synthesis of **4e** was carried out by the same procedure as that for **4a** except that V(N-2,6-$Cl_2C_6H_3$)(CH_2SiMe_3)$_3$ (299 mg, 0.633 mmol) was used and 2,6-$^tBuC_6H_4OH$ (111 mg, 0.739 mmol) was added in the place of 2,6-$F_2C_6H_3OH$. Yield: 372 mg (99%). ^{1}H NMR (C_6D_6): δ 0.13 (s, 18H, CH_2SiMe_3), 1.72 (s, 9H, ^tBu), 2.86 (br, 2H, CH_2SiMe_3), 2.93 (br, 2H, CH_2SiMe_3), 6.19 (t, 1H, J = 8.1, Ar-*H*), 6.81 (t, 1H, J = 7.6, Ar-*H*), 6.89 (m, 3H, Ar-*H*), 7.05 (d, 1H, J = 7.9, Ar-*H*), 7.24 (d, 1H, J = 7.6, Ar-*H*). ^{51}V NMR (C_6D_6): δ 584 ($\Delta\nu_{1/2}$ = 316 Hz). ^{13}C NMR (C_6D_6): δ 1.9 ($SiMe_3$), 30.5 (Me_3C−), 35.2 (Me_3C−), 123.6, 124.7, 125.2, 126.5, 127.4, 132.2, 165.4 (Ar).

NMR Experiments for Time Course in the Reaction of V(NAr′)(CH_2SiMe_3)$_3$ (Ar′ = C_6H_5, 2-MeC_6H_4, 2,6-$Me_2C_6H_3$, 2,6-$Cl_2C_6H_3$) with ArOH (Ar = 2,6-$F_2C_6H_3$, 2,6-$Cl_2C_6H_3$, 2,6-$Me_2C_6H_3$, 2,6-$^iPr_2C_6H_3$, 2-$^tBuC_6H_4$) in C_6D_6. The typical procedure is as follows. Into a C_6D_6 solution (ca. 0.6 mL) containing V(NC_6H_5)(CH_2SiMe_3)$_3$ (20.2 mg, 50 μmol), a C_6D_6 solution (ca. 0.4 mL) containing 2,6-$F_2C_6H_3OH$ (6.5 mg, 1.0 equiv) was added at 25 °C. The mixture was then monitored by both ^{1}H and ^{51}V NMR spectra after a certain period (10 and 40 min) to estimate the ratio (conversion) by the integration ratio of the starting material and the product.

NMR Experiments for Time Course in the Reaction of V(NAr′)(CH_2SiMe_3)$_3$ (Ar′ = C_6H_5, 2-MeC_6H_4, 2,6-$Me_2C_6H_3$ 2,6-$Cl_2C_6H_3$) with 2,6-$^tBu_2C_6H_3OH$ in C_6D_6. Typical procedure is as follows:

(i) Reaction of V(NC_6H_5)(CH_2SiMe_3)$_3$ with 1.0 equiv of 2,6-$^tBu_2C_6H_3OH$ at 25−60 °C. Into a C_6D_6 solution (0.4 mL) containing V(NC_6H_5)(CH_2SiMe_3)$_3$ (11 mg, 0.05 mmol) in J. Young NMR tubes, a C_6D_6solution (0.4 mL) containing 2,6-$^tBu_2C_6H_3OH$ (21 mg, 0.05 mmol) was added slowly at room temperature. The reaction mixture was monitored by ^{1}H and ^{51}V NMR at 20 min, 17 h, and 4 days. Then, the reaction mixture was heated at 60 °C and monitored by NMR spectra at 9, 31, and 50 h. The spectra are shown in the Supporting Information.[b]

(ii) Reaction of V(NC_6H_5)(CH_2SiMe_3)$_3$ with 3.0 equiv of 2,6-$^tBu_2C_6H_3OH$ at 25−60 °C. The reaction was conducted similar to the reaction with 1.0 equiv of 2,6-$^tBu_2C_6H_3OH$ except that the reaction was conducted at 25 °C for 6 days. The resultant mixture was monitored by ^{1}H NMR spectrum in C_6D_6. The spectra are shown in the Supporting Information.[b]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00531.

Selected NMR spectra for (NAr′)(CH_2SiMe_3)$_2$(OAr) [**1a−e**, **2a−e**, **3b,e**, **4a−e**; Ar′ = C_6H_5 (**1**), 2-MeC_6H_4 (**2**), 2,6-$Me_2C_6H_3$ (**3**), 2,6-$Cl_2C_6H_3$ (**4**); Ar = 2,6-$F_2C_6H_3$ (**a**), 2,6-$Cl_2C_6H_3$ (**b**), 2,6-$Me_2C_6H_3$ (**c**), 2,6-$^iPr_2C_6H_3$ (**d**), 2-$^tBuC_6H_4$ (**e**)], V(N-2-MeC_6H_4)(CH_2SiMe_3)$_3$, V(N-2,6-$Cl_2C_6H_3$)(CH_2SiMe_3)$_3$, and V(N-2,6-$Cl_2C_6H_3$)Cl_3; selected NMR spectra for monitoring the reaction of V(NAr′)(CH_2SiMe_3)$_3$ with ArOH (PDF)

Crystallographic analysis procedure, oak ridge thermal ellipsoid plot drawings and selected bond distances and angles, CIF and xyz files for V(N-2,6-$Cl_2C_6H_3$)-(CH_2SiMe_3)$_2$(O-2,6-$^iPr_2C_6H_3$) (**4d**, CCDC 1879594); computed Cartesian coordinates of all of the molecules for complex **4d** reported in this study (CIF)

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Files to be opened as a text file to read the coordinates or directly by a molecular modeling program such as Mercury (version 3.3 or later, http://www.ccdc.cam.ac.uk/pages/Home.aspx) for visualization and analysis (TXT)

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Notes

The authors declare no competing financial interest.

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ADDITIONAL NOTES

[a]Selected NMR spectra for V(NAr')$(CH_2SiMe_3)_2$(OAr) [**1a**–**e**, **2a**–**e**, **3b**,**e**, **4a**–**e**; Ar' = C_6H_5 (**1**), 2-MeC_6H_4 (**2**), 2,6-$Me_2C_6H_3$ (**3**), 2,6-$Cl_2C_6H_3$ (**4**); Ar = 2,6-$F_2C_6H_3$ (**a**), 2,6-$Cl_2C_6H_3$ (**b**), 2,6-$Me_2C_6H_3$ (**c**), 2,6-$^iPr_2C_6H_3$ (**d**), 2-$^tBuC_6H_4$ (**e**)] and structural analysis for **4d**, including CIF and xyz files, are shown in the Supporting Information. The crystallographic analysis data was also deposited in the Cambridge Crystallographic Data Centre (CCDC 1879594).

[b]Selected NMR spectra for monitoring the reaction of V(NAr')$(CH_2SiMe_3)_3$ with ArOH are shown in the Supporting Information. The conversions of V(NAr')$(CH_2SiMe_3)_3$ were estimated on the basis of integration ratios of dialkyl/trialkyl complexes in ^{51}V NMR spectra, and the ratios in the reaction with 2,6-$Cl_2C_6H_3OH$ were estimated by ^{1}H NMR spectra.

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